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Article *in* Spectroscopy Letters · January 2009

DOI: 10.1080/00387010903338335

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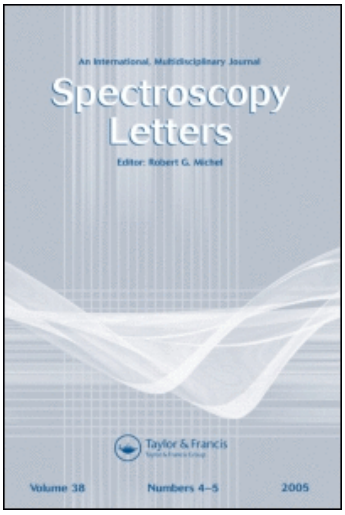

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

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Online publication date: 27 April 2010

To cite this Article Saraswathy, P. , Sunanda, K. , Aparna, S. and Raja Sekhar, B. N.(2010) 'Photoabsorption Spectra of Ammonia in 1050 to 2250 Å Region', Spectroscopy Letters, 43: 4, 290 — 297
To link to this Article: DOI: 10.1080/00387010903338335
URL: http://dx.doi.org/10.1080/00387010903338335

Spectroscopy Letters, 43:290–297, 2010

ISSN: 0038-7010 print/1532-2289 online
DOI: 10.1080/00387010903338335

Photoabsorption Spectra of Ammonia in 1050 to 2250 Å Region

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ABSTRACT Photo absorption spectrum of ammonia was investigated in the 1050 to 2250 Å region using synchrotron radiation from the Indian synchrotron light source, Indus-1. Photophysics beamline coupled to a gas phase experimental station was used to record ammonia spectrum. Experiments were carried out at different static pressures (0.02 to 20 mbar) of ammonia and its mixtures with inert gases. Extensive progressions of bands of Rydberg nature converging to the first ionization potential of ammonia, X^2A_2'' have been observed. Addition of rare gas enhanced the Rydberg band absorption intensities especially in the 1050 to 1600 Å region. The $6sa_1'$ (F''')- $\leftarrow$ X and $5pe'(F'') \leftarrow 1a''_2$ Rydberg series, not reported earlier by VUV absorption spectroscopy, is observed in the present studies and are presented along with their vibrational assignments. The G state reported to be a $6de''$ Rydberg state, is more likely a $7sa_1'$ Rydberg state, verified from the quantum defect calculations. Details of the analysis and results obtained are discussed in this paper.

KEYWORDS ammonia, electronic spectrum, photo absorption, photophysics beamline, rydberg states, vacuum ultraviolet

INTRODUCTION

Photo-absorption spectroscopy of atoms and molecules in the vacuum ultraviolet region using synchrotron radiation has found many important applications in the field of astrophysics, environmental sciences, etc., by providing accurate information on the absorption cross sections, high lying valence and Rydberg states, ionization potentials, photo-dissociation, fluorescence, etc.[1] The observation of ammonia (NH_3) in planetary atmospheres, comets and interstellar media has brought forward many recent studies on ammonia and its isotopic variants. There are several experimental[2] and references therein] and theoretical studies[3,4] on the photo-absorption spectrum of ammonia which has provided text book examples of several molecular phenomena such as Jahn-Teller effect, Coriolis splitting, vibrational pre-dissociation, inversion doubling, non-planar to planar transitions, etc. Much of the earlier spectroscopic work used conventional UV and VUV gas phase absorption to elucidate the electronic spectrum. Complementary techniques such as photoelectron spectroscopy,[5] photo

Received 20 July 2009;
accepted 15 September 2009.

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dissociation studies,[6] multi photon ionization (MPI), resonance enhanced multi photon ionization (REMPI),[7–10] electron impact spectroscopy (EIS),[11] electron energy loss spectroscopy (EELS)[12] and fluorescence excitation spectroscopy (FEX)[13] carried out with lasers and synchrotron radiation have offered unique advantages for the analysis of the excited states and contributed much to the better understanding of the molecule regarding the molecular symmetries, ionization potentials, dissociation, etc. Using monochromatised synchrotron radiation, the absolute photo-absorption, photo-dissociation and photo-ionization cross sections of ammonia and four deuterated isotopologues have been measured in the 10–25 eV region by Edwardsson et al.[14] B. M. Cheng et al.[15] in their recent paper on photo absorption cross sections of ammonia and four deuterated isotopologues reported absorption cross-sections of A-X and B-X systems in the region 140–220 nm. Photo absorption cross section studies on ammonia and its isotopic variants were carried out by Wu et al.[16] in the 110–144 nm wavelength region using synchrotron radiation.

The present work deals with the results of VUV gas phase absorption experiments carried out on ammonia using photo physics beam line in the wavelength range of 1050 to 2250 Å, at Indus-1, a 450 MeV synchrotron radiation source, at Raja Ramanna Centre for Advanced Technology (RRCAT), Indore, India.[17] The absorption experiments were performed with an average resolving power of 1000. Lithium fluoride window used in the beamline decided the high to energy cut-off of the beamline (~1050 Å). Spectra of ammonia were recorded under different pressure conditions to obtain spectra with optimum signal to noise ratio. Addition of rare gases, Xe and Kr helped in enhancing absorption intensities at certain pressures. An extensive analysis of NH_3 absorption spectrum recorded has been carried out and the results are presented in this paper.

Experimental Setup for Gas Phase Absorption Spectroscopy

A six way stainless steel cross of 25 cm length, with four 35CF and two 63CF ports for pumping, absolute pressure measurement gauges, valves and sample introduction, light entry and light exit, served as the absorption cell. The cell is evacuated to pressures less than 10^{-5} mbar using a turbo molecular pumping station. The sample to be studied is kept in a glass bulb connected to the cell through a set of shut-off valves to fill, hold and control the sample pressure during experiments. Prior to filling ammonia sample in the gas cell, it is purified from absorbed atmospheric gases by repeated freeze-pump-thaw technique. A capacitance gauge mounted on the cell facilitates accurate pressure measurement in the range 0.001 mbar to 100 mbar. Detection of the transmitted light is done by a UV-visible sensitive photomultiplier with a sodium salicylate coated quartz window kept in front. Data is recorded through a PC based data acquisition and control system developed in house. The blank (reference) spectrum (I_0) and sample spectrum (I) recorded as a function of wavelength was normalized with respect to the synchrotron beam current and absorbance spectra $\ln(I_0/I)$ versus wavelength was plotted. The resolution of the beamline determined by recording the spectra of xenon gas of spectroscopic grade was found to be 1.5 Å at 1469 Å Xe line. The spectrum of ammonia was recorded at different pressures ranging from <0.001 to 20 mbar, with and without the addition of Kr or Xe. The spectrum with xenon was also utilized to calibrate the observed ammonia spectrum.

RESULTS AND DISCUSSIONS

The absorption spectrum of NH_3 in the 1050 to 2250 Å region is shown in Fig. 1. The spectrum is very complex. All the observed excited electronic states of ammonia are Rydberg in nature. The observed excited electronic states of ammonia below the first ionization energy are formed by the promotion of an electron from the doubly occupied $3a_1$ nitrogen lone pair orbital in pyramidal ground state to Rydberg orbitals with principal quantum number $n \geq 3$, resulting in states with planar equilibrium geometries (D_{3h}). As a result of the change in geometry during excitation, each electronic transition appears with long progressions associated with excitation of out of plane mode ν_2. This is evident from the experimental observation of long progressions involving the ν_2 frequency. The 0–0 transition is non-vertical and the strongest bands involve v′ around 5 to 7. All of the excited states possess either A or E symmetry.[2]

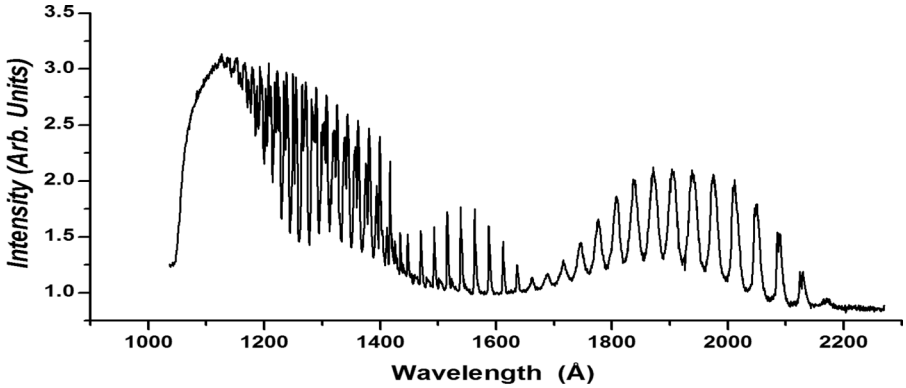

FIGURE 1 **Photo absorption spectrum of ammonia.**

The spectrum of ammonia was recorded at pressures ranging from 0.001 to 20 mbar. A good spectrum with considerable signal to noise ratio and well below saturation limit was obtained for the entire region of 1050 to 2250 Å when ammonia pressure was ~0.001 mbar. At pressures above 5 mbar, the spectrum showed saturation, except for the few hot bands appearing at the higher wavelength side of A-X system. It was observed the spectra were sharp and intense with addition of rare gases (krypton or xenon) in the pressure ranging from 2 mbar to 10 mbar. At moderate pressures of rare gas (5 mbar with partial pressure of ammonia maintained at ~0.001 mbar), the sharpness of bands as well as band intensities enhanced in the region below 1600 Å and the observed bands could be easily assigned to higher members of the Rydberg series.

Fourteen electronic excited states were identified (C state is not an independent state) and in the order of their energy, along with their molecular symmetries are given in Table 1. The vibrational progressions associated with these electronic states are listed in Table 2. A brief description of the observed transitions assigned to different Rydberg series is given below.

$nsa'_1(^1A_2'') \leftarrow X1a''_2$ Series

The first excited state of ammonia, $3sa'_1(^1A_2'')A \leftarrow 1a''_2$ has been well characterized experimentally as an allowed Rydberg transition with an intensity maximum at $v' = 6$ at 1938 Å. The bands are broad as expected for transition to $^1A''_2$ symmetry. At high pressures of ammonia (20 mbar) hot bands appear at the higher wavelength side of 0–0 band. These bands (1–0, 2–0) have been listed in the Table 2 along with other members. The second transition of this Rydberg series, $4sa'_1(^1A_2'')D' \leftarrow 1a''_2$ is relatively weak and appears as a shoulder to D state. The third and fourth transitions of this series $5sa'_1(^1A_2'')E'' \leftarrow 1a''_2$ and $6sa'_1(^1A_2'')$ $F''' \leftarrow 1a''_2$ are also listed in the Table 2. Although the $6sa'_1(^1A_2'')$ $F''' \leftarrow 1a''_2$ transition was observed in EELS studies by Locht et al.,[5] it has been reported for the first time in photo absorption in the present studies. Following the nomenclature used for the other Rydberg states, this transition has been designated as $F''' \leftarrow X$. It may also be mentioned here that the members of the P2 series reported as unassigned in the studies of Wu et al.[16] go as the higher members of the $F''' \leftarrow X$ transition. The assignment of the band

TABLE 1 **Observed Electronic States of Ammonia**

State	Molecular orbital (Rydberg notation)	Symmetry	Energy (cm^{-1})
X	$(1s_N)^2\ (a_1')^2\ (e')^4\ (a_2'')^2$	$^1A_1'$	Ground state
A	$(1s_N)^2\ (a_1')^2\ (e')^4\ (a_2'')\ (3sa_1')$	$^1A_2''$	45677
B	$(1s_N)^2\ (a_1')^2\ (e')^4\ (a_2'')\ (3pe')$	$^1E''$	58750
*C	$(1s_N)^2\ (a_1')^2\ (e')^4\ (a_2'')\ (3pe')$	$^1E''$	59193
C′	$(1s_N)^2\ (a_1')^2\ (e')^4\ (a_2'')\ (3pa_2'')$	$^1A_1'$	63437
D	$(1s_N)^2\ (a_1')^2\ (e')^4\ (a_2'')\ (3de'')$	$^1E'$	69319
D″	$(1s_N)^2\ (a_1')^2\ (e')^4\ (a_2'')\ (3da_1')$	$^1A_2''$	69570
D′	$(1s_N)^2\ (a_1')^2\ (e')^4\ (a_2'')\ (4sa_1')$	$^1A_2''$	69659
D‴	$(1s_N)^2\ (a_1')^2\ (e')^4\ (a_2'')\ (4pe')$	$^1E''$	71567
E″	$(1s_N)^2\ (a_1')^2\ (e')^4\ (a_2'')\ (5sa_1')$	$^1A_2''$	73312
E‴	$(1s_N)^2\ (a_1')^2\ (e')^4\ (a_2'')\ (4da_1')$	$^1A_2''$	73394
E	$(1s_N)^2\ (a_1')^2\ (e')^4\ (a_2'')\ (4de'')$	$^1E'$	74709
F″	$(1s_N)^2\ (a_1')^2\ (e')^4\ (a_2'')\ (6pe')$	$^1E''$	75686
F	$(1s_N)^2\ (a_1')^2\ (e')^4\ (a_2''))\ (5de'')$	$^1E'$	77289
F‴	$(1s_N)^2\ (a_1')^2\ (e')^4\ (a_2'')\ (6sa'_1)$	$^1A_2''$	77378
G	$(1s_N)^2\ (a_1')^2\ (e')^4\ (a_2'')\ (7sa'_1)$	$^1A_2''$	78272

*Vibrational component of B.

TABLE 2 Vibrational Wave Numbers of the Observed Progressions in Ammonia Spectra

	A-X		D′-X		E″-X		F‴-X	
v′	ν (cm^{-1})	λ (Å)	ν (cm^{-1})	λ (Å)	ν (cm^{-1})	λ (Å)	ν (cm^{-1})	λ (Å)
0	46104	2169	70097	1427	73792	1355	77777	1286
1	47082	2124	70959	1409	74773	1337	78760	1270
2	47985	2084	71920	1390	75782	1320	79864	1252
3	48847	2047	72826	1373	76821	1302	80632	1240
4	49768	2009	73784	1355	77889	1284	81611	1225
5	50679	1973	74796	1337	78986	1266	82617	1210
6	51612	1938	75808	1319	80112	1248	83637	1196
7	52531	1904	76849	1301	81266	1231	84594	1182
8	53492	1869			82450	1213	85638	1168*
9	54461	1836			83663	1195	86681	1154*
10	55395	1805			84904	1178	87717	1140*
11	56362	1774					88728	1127*
12	57301	1745					89900	1112
13	58256	1717					90869	1100
14	59229	1688						
15	60165	1662						
16	61097	1637						
(1,0)#	45372	2204						
(2,0)#	44623	2241						

	B-X		C-X(&)		D‴-X		F″-X	
	ν (cm^{-1})	λ (Å)	ν (cm^{-1})	λ (Å)	ν (cm^{-1})	λ (Å)	ν (cm^{-1})	λ (Å)
0	59228	1688			69979	1429	76198	1312
1	60165	1662	60679	1648	70921	1410	77112	1297
2	61097	1637	61531	1625	71785	1393	78142	1280
3	62059	1611	62512	1599	72767	1374	79175	1263
4	63033	1586	63508	1574	73694	1357	80177	1247
5	64039	1562	64537	1549	74684	1339	81207	1231
6	65058	1537	69614	1524	75697	1321	82237	1216
7	66069	1514	66567	1502	76784	1302		
8	67112	1490	67509	1481	77919	1283		
9	68133	1468	68476	1460				
10	69211	1445	69447	1440				
11	70290	1423	70413	1420				
12	71378	1401	71399	1401				

	D-X		E-X		F-X		G-X	
	ν (cm^{-1})	λ (Å)	ν (cm^{-1})	λ (Å)	ν (cm^{-1})	λ (Å)	ν (cm^{-1})	λ (Å)
0	69802	1433	75273	1328	77802	1285	78856	1268
1	70693	1415	76115	1314	78660	1271	79802	1253
2	71620	1397	77026	1298	79662	1255	80788	1238
3	72572	1378	78096	1280	80470	1243	81826	1222
4	73549	1360	79081	1265	81609	1225	82853	1207
5	74527	1342	80063	1249	82621	1210	83862	1192
6	75560	1324	81129	1233	83681	1195	84875	1178
7	76599	1305	82160	1217	84727	1180	85919	1164
8	77627	1288	83186	1202	85743	1166	86985	1150
9	78660	1271	84238	1187	86790	1152	88072	1135

(*Continued*)

TABLE 2 Continued

	D-X		E-X		F-X		G-X	
	ν (cm^{-1})	λ (Å)	ν (cm^{-1})	λ (Å)	ν (cm^{-1})	λ (Å)	ν (cm^{-1})	λ (Å)
10	79752	1254	85284	1173	87862	1138	89213	1121
11	80811	1238	86326	1158	88962	1124	90054	1110
12	81900	1221	87377	1144			91035	1098
13							92175	1085

	C′-X		D″-X		E‴-X	
	ν (cm^{-1})	λ (Å)	ν (cm^{-1})	λ (Å)	ν (cm^{-1})	λ (Å)
0	63901	1565	69979	1429	73862	1354
1	64854	1542	70921	1410	74860	1336
2	65750	1521	71785	1393	75859	1318
3	66690	1499	72767	1374	76857	1301
4	67680	1478	73694	1357	77856	1284
5	68631	1457	74684	1339	78854	1268
6	69585	1437	75697	1321	79853	1252
7	70531	1418	76784	1302	80851	1237*
8	71530	1398	77919	1283	81850	1222*
9					82848	1207*
10					83847	1193*
11					84845	1179*
12					85844	1165

#hot bands; *P2 series of Ref.[16]; (&)Vibrational numbering relative.
*P1 series of Ref.[16].

system at 1278 Å (78272 cm^{-1}) as next member of this series, $7sa'_1(^1A_2'')G \leftarrow 1a''_2$ was reported,[14,18] Leach et al.[13] suggested this band system as $6de''(^1E'')G \leftarrow X1a''_2$ transition, since they are sharp and intense compared to the broad and diffuse nature of the $nsa'_1(^1A_2'') \leftarrow 1a''_2$ series. Quantum defect calculations carried out for $nde''(^1E'') \leftarrow 1a''_2$ series give a value of 0.68 for δ somewhat higher than the value expected for the d series. The G-X transition has been taken as $7sa'_1(^1A_2'') \leftarrow 1a''_2$ in the present studies with a δ value 1.68 comparable with s state.

$npe'(^1E'') \leftarrow X1a''_2$ Series

Three members of the series $npe'(^1E'')$ are observed in the present investigations. The first band system observed in the 1800 to 1500 Å region, consisting of long progression of sharp bands is assigned as $3pe'(^1E'')B \leftarrow 1a''_2$. This is a forbidden transition, observed via Herzberg-Teller vibronic coupling. It is a perpendicular transition with an intensity maximum at $v' = 5$ at 1562 Å. Vibronic states of B are degenerate and the degeneracy is of electronic nature. Another weak band system lying in the same region as B-X, designated as $3pe'(^1E'')C \leftarrow 1a''_2$ state results from the forbidden component of the excitation of a combination of vibrational levels of B state. By multi photon ionization spectroscopy, Glownia et al.[8] have suggested that C state is due to weak Jahn-Teller effect. The origin of C state should be close to B. Considering the intensity of band maxima at around $v' = 5$, vibrational numbering of the observed bands of C-X transition observed was carried out are reported in Table 2. Table 3 gives the vibrational constants obtained for the C-X system. The next two members of these series $4pe'(^1E'')D''' \leftarrow 1a''_2$ and $5pe'(^1E'')F'' \leftarrow 1a''_2$ previously reported as observed only in MPI[8,10] studies are observed, though weakly in the present VUV absorption studies. The $4pe'(^1E'')D''' \leftarrow 1a''_2$ series is reported by Wu et al.[16] studies in photo absorption, the $5pe'(^1E'')F'' \leftarrow 1a''_2$ series is been reported for the first time.

$npa_2''(^1A_1') \leftarrow X1a''_2$ Series

Apart from the C system, another weak progression in the vicinity of B state has been observed

TABLE 3 Vibrational Constants (cm^{-1}) and Rydberg Constants of Ammonia

n	State	T_e	ω_e	$\omega_e^{\&}$	$\omega_e x_e$	$\omega_e x_e^{\&}$	n^*	δ
$^1A_2''(sa'_1)$								
3	A	45677	902.98	884.	2.062	6.9	1.73	1.27
4	D′	69659	861.22	927	13.02	12.7	2.96	1.04
5	E″	73312	951.84		14.492		3.52	1.48
6	F‴	77378	918.36		6.350		4.79	1.21
7	G	78272	927	949	7.88	11.1	5.3	1.7
$^1E''(pe')$								
3	B	58750	923.49	906	6.952	15.7	2.16	0.84
	C	59193	943		4.9			
4	D″	71567	921.87	924	11.72	22.9	3.22	0.78
5	F″	75686	969.05		6.167		4.12	0.88
$^1A_1'(pa_2'')$								
3	C′	63437	926		2.8		2.4	0.60
$^1E'(de'')$								
3	D	69319	903.67	890	8.30	18.8	2.92	0.0758
4	E	74709	949.261	913	5.39	18.3	3.84	0.1603
5	F	77288	918.23	917	8.55	19.8	4.75	0.25
6	(G)	78272	927	949	7.88	11.1	5.32	0.6824
$^1A_2''(da_1')$								
3	D″	69570	859		13.39		2.95	0.05
4	E‴	73394	972		3.77		3.54	0.46

which is assigned to $3pa_2''(^1A_1')C' \leftarrow 1a''_2$ series. For quite sometime, C and C′ states were thought to be same but a high resolution study of this transition,[2] identified C′ to be an independent state lying close to B state. This is found to be a parallel type transition, not expected for a component of B. Harshbarger[11] in his study of electron impact spectroscopy of ammonia compared the relative intensities of the C′-X and B-X system and found that the intensities of peaks in the two progressions change markedly as a function of energy of the incident beam. This provided valid proof to suggest that C′ state is a separate excited electronic state. Nieman and Colson[9] observed this transition in MPI. A part of

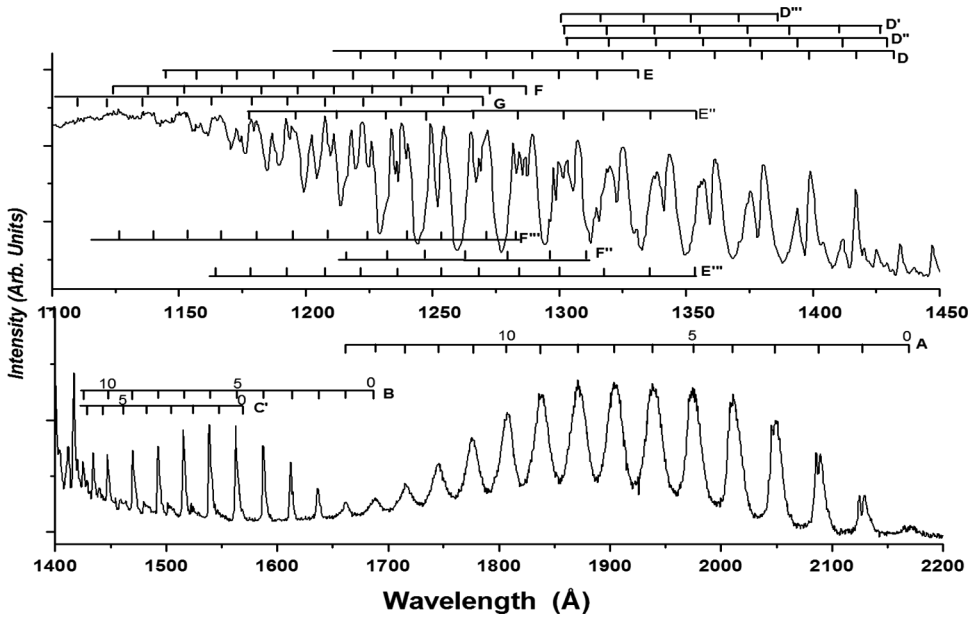

FIGURE 2 Ammonia spectrum marked with all the observed Rydberg states.

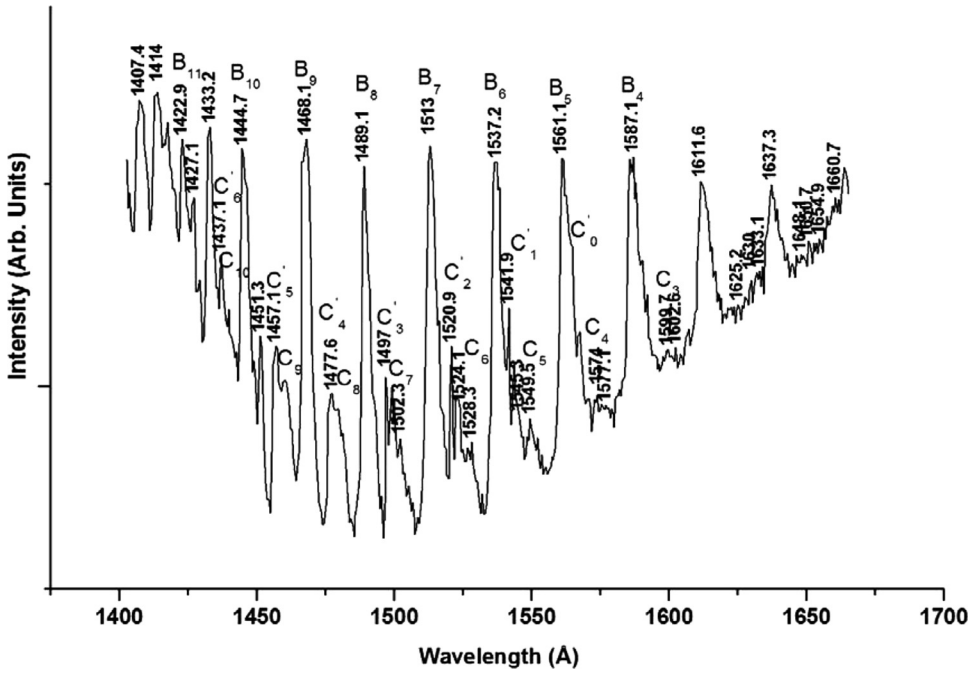

FIGURE 3 Part of ammonia spectrum showing B, C and C′ states.

the spectrum, recorded with a mixture of Kr and ammonia (in the ratio 5:0.05 mbar) is shown in Figure 3 showing the C and C′ positions. Both of these systems (C and C′) appeared with observable intensity in spectra where rare gas was added to ammonia. The frequencies and wave numbers of the bands are given in Table 2. Higher members of the $npa_2''(^1A_1')$ series were not observed.

$Nde''(^1E'') \leftarrow X1a''_2$ Series

Three intense transitions assigned to $3de''(^1E'')D \leftarrow 1a''_2$, $4de''(^1E'')E \leftarrow 1a''_2$ and $5de''(^1E'')F \leftarrow 1a''_2$ are observed in the 1400–1100 Å region. Of these, the most intense is the D-X transition. The G-X transition previously taken as belonging to this series, is assigned to sa'_1 Rydberg series on the basis of quantum defect calculations. The bands identified compare well with those reported by Wu et al.[16]

$nda_1'(^1A_2'') \leftarrow X1a''_2$ Series

Two weak progressions of the $nda_1'(^1A_2'') \leftarrow 1a''_2$ are observed in the present studies. $3da_1'(^1A_2'')D'' \leftarrow X1a''_2$ and $4da_1'(^1A_2'')E''' \leftarrow X1a''_2$ have been identified. The P1 series listed as unassigned in Wu et al.[16] are assigned as the higher members of the $E''' \leftarrow X$ transition. The D′-X (1428 Å) and D″ (1429 Å) whose origins are degenerate, are observed only in VUV photo absorption experiments. The D″ series is weak and appear as shoulder on the higher wavelength side of the D′ series. Similarly, E″-X (1334 Å) and E‴-X (1331 Å) appear in gas phase photo absorption technique[8] and are also degenerate.

The authenticity of the weak spectral lines have been confirmed from many recordings of the spectrum at different pressures. The data obtained in the present photo absorption studies compare well with the values reported in literature[15,16] for photo absorption studies. The data available from other technique such as MPI, REMPI, EELS[3–14] were useful for cross-checking the assignment of the data.

Vibrational constants ω_e' and $\omega_e'x_e'$ for the excited states for each progression are obtained by fitting the observed bands to a standard formula

$$\nu_{v'} = \nu_e + \omega_e'(v + 1/2) - \omega_e'x_e'(v + 1/2)^2. \qquad (1)$$

In the present calculations ν_e corresponds to the value of the 0–0 band. The values obtained for all the transitions are listed in Table 3, along with values reported in literature. It is observed that in each of these transitions the vibrational intervals increase with v′. This could be due to the positive value of anharmonicity ($\omega_e x_e$) in the upper state. As can be seen from the table, the anharmonicity factor $\omega_e x_e$ is positive for the excited states of ammonia.

To calculate the quantum defect, the Rydberg series observed for ammonia belonging to ns, np, and nd series have been fitted using Rydberg formula:

$$n^* = n - \delta = [R/(IE - E)]^{1/2} \quad (2)$$

where, n^* is the effective quantum number and is a primary parameter applicable for the assignment of a progression in a Rydberg transition, n is the principal quantum number, δ is the quantum defect, IE is the ionization energy, E the energy of the observed electronic state and R is the Rydberg constant. R in the present studies is taken as $109733.80\,cm^{-1}$ and ionization energy IE as $82010\,cm^{-1}$.[16] The effective quantum numbers along with quantum defects are listed in Table 3.

CONCLUSION

The VUV absorption spectrum of ammonia was recorded in the region of 1050 to 2200 Å using synchrotron radiation on the photophysics beam line of Indus-1. With the introduction of xenon (total pressure of ammonia and xenon being 5 mbar) vibrational features in the <1600 Å region were enhanced. Fourteen Rydberg states have been identified and states assigned. The spectral features agree well compared with earlier workers. The hitherto unassigned series P1 and P2 are assigned as higher members of the $6sa'_1\,E''' \leftarrow X$ and $4da_1'E''' \leftarrow X$ transitions, respectively. From quantum defect calculations it is surmised that the transition previously assigned as $6de''(^1E')$-$1a_2''$ is in fact $7sa'_1$-$X1a_2''$. The $6sa_1'(F''') \leftarrow X$ and $5pe'(F'') \leftarrow 1a''_2$ Rydberg series reported for the first time by VUV absorption spectroscopy and they are presented with their vibrational assignments.

ACKNOWLEDGMENTS

The authors thank Dr. S. C. Sabharwal, Head, Spectroscopy Division for his encouragement during the course of this work. We gratefully acknowledge the help rendered by the members of our divisional workshops. We thank the electronic section for the indigenously developed DAS.

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